

# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-020458

(43)Date of publication of application : 23.01.2002

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(51)Int.Cl.

C08G 59/40  
C08L 63/00  
C08L101/10

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(21)Application number : 2000-206521

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(22)Date of filing : 07.07.2000

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## (54) ROOM TEMPERATURE-SETTING COMPOSITION

### (57)Abstract:

**PROBLEM TO BE SOLVED:** To obtain a room temperature-setting composition which contains an organic polymer having at least one reactive silicon-containing group as the main component and has a sufficient adhesiveness even to the steel plate coated with an acrylic resin or with a fluororesin by an electrophoretic deposition process, or to the cured product of a sealant such as a silicone sealant.

**SOLUTION:** This room temperature-setting composition comprises (A) 100 pts. mass of an organic polymer which has at least one silicon-containing group, has a hydroxyl group or a hydrolyzable group bonding to the silicon, and can crosslink by forming a siloxane bond, (B) 1-50 pts. mass of an epoxy resin, (C) 0.1-30 pts. mass of an oxazolidine compound, (D) a silanol condensation catalyst, and (E) an amine promoter.

## \* NOTICES \*

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

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CLAIMS

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[Claim(s)]

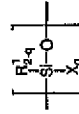
[Claim 1](A) Organic polymer 100 mass part which has a hydroxyl group or a hydrolytic basis combined with a silicon atom, and has at least one silicon content group which can construct a bridge by forming a siloxane bond, (B) A room-temperature-curing nature constituent containing one to epoxy resin 50 mass part, the (C) oxazolidine compound 0.1 - 30 mass parts, the (D) silanol condensation catalyst, and (E) amine system co-catalyst

[Claim 2](F) (1)2-ethylhexanoic acid, (2) The room-temperature-curing nature constituent containing at least one oxazolidine ring breakage accelerator chosen from a group which consists of a mixture or an addition of ORUTOGI acid ester and (3) ORUTOGI acid ester, and a p-toluenesulfonic-acid monoisocyanate according to claim 1.

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[Translation done.]





$[0019]_q$  which can be boiled and set does not need to be the same.  $r$  is an integer of 0, or 1~19. The basis shown is mentioned.

basis shown is incorrect.

alkoxy group.

[0021] This hydrolytic basis and hydroxyl group can be combined with one silicon atom in the 1-3 ranges, and, as for (p+q), it is preferred that it is the range of 1-5. When a hydrolytic basis and a hydroxyl group join together in [two or more] a reactive silicon group, they may be the same or differ.

[0022]The number of silicon atoms which form this reactive silicon group may be one, they may be two or more pieces, and are following formulas especially. [0023]

[0023] the number of elements being written to two or more pieces, and are following formulas especially. [0023]

[Formula 3]



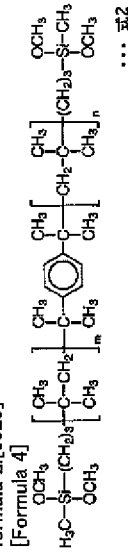
[0024](R<sup>2</sup>, X, and p are the same as the above among a formula.) — the reactive silicon group shown — acquisition — since it is easy, it is desirable.

acquisition—since it is easy, it is desirable. [0025] 1–5 reactive silicon groups exist preferably in [at least one] one molecule of an organic polymer. The number of the reactive silicon groups contained in a molecule becomes difficult to reveal an adhesive property in less than one piece.

[0026] The reactive silicon group may exist in the end of the chain of (A) organicity polymer, may exist in the inside, and may exist in both. When especially a reactive silicon group exists in a molecular terminal, since the effective network chain density of the organic polymer component contained in the hardened material formed eventually increases, it is desirable. These may be used alone and may be used together two or more sorts.

alone and may be used against the more serious [0027]The number average molecular weight of this (A) organicity polymer especially an isobutylene system polymer, or a hydrogenation polybutadiene system polymer is preferred from points — it is desirable still more preferred that it is 500 to about 100000, and it is easy to deal with about 1000 to 30000 thing which is liquefied or has mobility.

[0028] A concrete manufacturing method of (A) organicity polymer explained above is indicated in detail to JP H8-41360, A. Specifically as a (A) organicity polymer explained above, it is the following formula 2 [0029]



[0030]EPION (made by Kaneka Corp.) (m and n are indicated to be to the integer of 0, or 1-20 and 1-20) is illustrated suitably.

[C31H47N3O7] it can have polyether and/or polyester which are obtained by the method currently indicated by JP, S61-18569 B as a (A) organicity polymer in a main chain, and the modified silicone resin which has a hydrolytic silicon group in a molecular terminal can also be used conveniently. Specifically, commercial MS polymer (made by Kaneka Corp.) is illustrated suitably. As a (A) organicity polymer, it has polyether and a polyester group in a main chain, and the silanizing polysulfide polyether polymer of a description, etc. can be illustrated to JP, H8-134168 A which introduced the hydrolytic silyl group into the OH radical or the sulfinhydril group of the end.

into the OH radical or the sulfonyl group or the end.

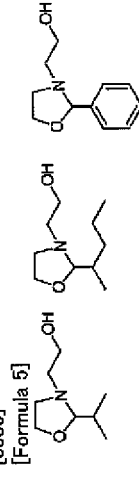
[ which has an average of one or more epoxy groups in 1 intramolecular ]. Average value of an epoxy group of 1 intramolecular refers to a value which broke the sum total of a molecular weight of an epoxy resin by the sum total of a weight per epoxy equivalent here. Specifically, various isomers of triglycidyl ether diaminodiphenylmethane, triglycidyl p-aminophenol, a triglycidyl m-aminophenol, and triglycidyl amino cresol are mentioned as an epoxy resin which uses amines as a precursor. Phenols as an epoxy resin used as a precursor A bisphenol A type epoxy resin, Bisphenol F type epoxy resin, a bisphenol smooth S form epoxy resin, phenol novolak type epoxy resin, cresol novolak type epoxy resin, a bisphenol novolak type epoxy resin, etc., are mentioned.

A polysulfide modified epoxy resin which uses as a main chain a polysulfide skeleton expressed with the following formula— $(C_2H_4OCH_2OC_2H_4S_n)_n$ —( $n$  is an integer of 1–5 among a formula.) is also used suitably. As for an example of this polysulfide modified epoxy resin, Flep 50 by the Toray Industries thiolol company, Flep 60, and Flep 65 grade are mentioned. In this invention, it is independent about various above-mentioned epoxy resins, or two or more sorts can be mixed and used. Since compatibility and the separability of (A) organioity polymer and the (B) epoxy resin participate in superiority or inferiority of adhesion manifestation nature, it is also useful by using together two or more sorts of epoxy resins to adjust both compatibility and separability to a suitable grade, so that it may mention later.

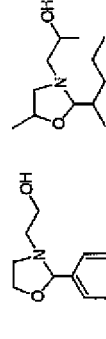
may mention that:  
[0033]Content of the (B) epoxy resin in a room-temperature-curing nature constituent of this invention is 1 – 50 mass part to (A) organicity polymer 100 mass part, and it is preferred that it is 1 – 30 mass part. The physical properties of an organic polymer are not spoiled as it is this range.

[0034] The (C) oxazolidine compound used for this invention is a compound which has the heterocycle of a saturated five-membered ring containing oxygen and nitrogen, and is a compound which has an oxazolidine ring which carries out ring breakage under existence of humidity (water). Specifically, N-hydroxyalkyl oxazolidine and its polysiocyanate addition, oxazolidine silyl ether, carbonate oxazolidine, ester oxazolidine, etc. are mentioned.

ester, oxazoline, etc. are mentioned.



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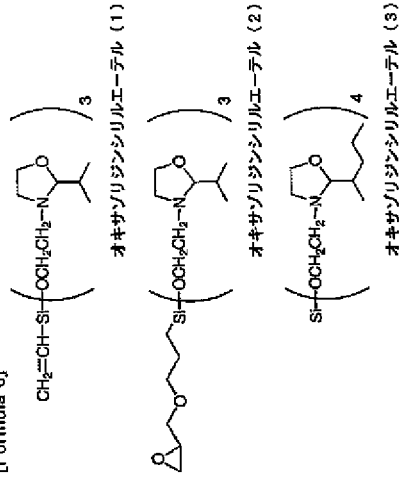
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オキソリジン (4)

[0037] Oxazolidine silyl ether Above-mentioned N-hydroxyalkyl oxazolidine, Trimethoxysilane, a tetramethoxy silane, triethoxysilane, It is obtained by a reaction with alkoxy silane, such as dimethoxy dimethylsilane, vinyltrimethoxysilane, vinyltriethoxysilane, gamma-glycidyloxypropyltrimethoxysilane, and dimethylsilane.

gamma-glycidyloxy propyltriethoxysilane. By making a titanium alkoxide, aluminum alkoxide, or divalent Sn into a catalyst, this reaction is 40 \*\* - 160 \*\*, and is especially performed at 80 \*\* - 140 \*\* preferably.

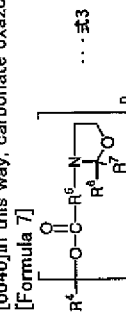
[0038]The example of oxazolidine silyl ether is shown below.

[Formula 6]



[0039]Carbonate oxazolidine etc. from which carbonate oxazolidine is obtained by a method of JP,H5-117252,A, for example are mentioned. Hydroxyalkyl oxazolidine and diaryl carbonate, such as the hydroxyalkyl oxazolidine (1) above-mentioned [ carbonate oxazolidine ] for example, it can obtain by making carbonate, such as dimethyl carbonate and dipropylene carbonate, react using polyhydric alcohol, such as a diethylene glycol and glycerin. 60-160 \*\* of this reaction is preferably performed at temperature of the range of 100-140 \*\*, for example under existence of transesterification catalysts, such as sodium methylate. As for an addition of a catalyst, it is preferred that it is 50-1000 ppm to the total quantity of hydroxyalkyl oxazolidine, carbonate, and polyhydric alcohol.

[0040]In this way, carbonate oxazolidine prepared is expressed with the following formula 3.

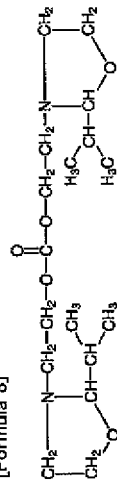


(n is an integer of 1-10 among a formula, and R<sup>4</sup> and R<sup>5</sup> are the organic groups of 1-8 carbon numbers independently respectively.) R<sup>6</sup> and R<sup>7</sup> are a hydrogen atom or an organic group of 1-8 carbon numbers independently respectively.

The following carbonate oxazolidine (1) is among one example of a compound expressed with the formula 3.

[0041]

[Formula 8]



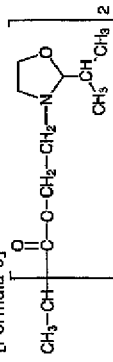
カーボネートオキサゾリジン (1)

[0042]As ester oxazolidine, various ester oxazolidine, such as ester oxazolidine obtained by the method of the US,3661923,B gazette and the US,4138545,B gazette, can be used, for example. For example, it can obtain by a reaction with low-grade alkyl ether of above-mentioned hydroxyalkyl

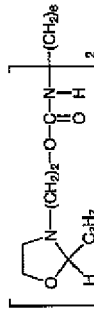
oxazolidine (1), dicarboxylic acid, or polycarboxylic acid. Specifically, the following ester oxazolidine (1) is mentioned. Commercial items, such as the hardener OZ by a Beyer company shown by the following ester oxazolidine (2), can also be used.

[0043]

[Formula 9]



エステルオキサゾリジン (1)

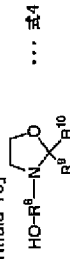


エステルオキサゾリジン (2)

[0044]May use the oxazolidine compound which has three or more oxazolidine rings into one molecule, and this compound, it compounds as a compound which has three or more oxazolidine rings in one molecule by reacting N-hydroxyalkyl oxazolidine and the polyisocyanate compound which are expressed with the following formula 4.

[0045]

[Formula 10]



[0046]R<sup>8</sup> is a divalent aliphatic hydrocarbon group which has the straight chain shape or the branched chain of the carbon numbers 2-3, for example, shows an alkylene group, an alkenylene group, and alkynylene group here. R<sup>9</sup> and R<sup>10</sup> show the univalent hydrocarbon group of a hydrogen atom or the carbon numbers 1-20 independently respectively. N-hydroxyalkyl oxazolidine expressed with the above-mentioned formula 4 is compounded by a method more publicly known than corresponding aldehyde or ketone, and N-hydroxy alkylamine.

[0047]As aldehyde, formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, isobutyraldehyde, a valeraldehyde, 2-methylbutyraldehyde, 3-methylbutyraldehyde, hexylaldehyde, 2-methylpentylaldehyde, Aliphatic aldehyde, such as octyl aldehyde and 3,5,5-trimethylhexylaldehyde; Benzaldehyde, Methylbenzaldehyde, trimethyl benzaldehyde, ethylbenzaldehyde, Aromatic aldehyde [ such as isopropylbenzaldehyde, isobutylbenzaldehyde, methoxy benzaldehyde, and dimethoxybenzaldehyde and trimethoxy benzaldehyde, ]; etc. are preferred. As ketone, acetone, methyl ethyl ketone, methyl propyl ketone, Methyl isopropyl ketone, a diethyl ketone, methyl butyl ketone, methyl isobutyl ketone, methyl-t-butyl ketone, diisobutyl ketone, cyclopentanone, cyclohexanone, etc. are preferred.

[0048]As N-hydroxy alkylamine, bis-N-(2-hydroxyethyl) amine, bis-N-(2-hydroxypropyl) amine, and N-(2-hydroxyethyl)-N-(2-hydroxypropyl) amine are preferred.

[0049]Although above-mentioned aldehyde or ketone, and hydroxy alkylamine react with this molar quantity of nitrogen corresponding to the number of mols of aldehyde or ketone, it is preferred to use aldehyde or ketone superfluously in 1.01-1.5. It is the range of 1.01-1.1 especially preferably. It is because separation with output is difficult for N-hydroxy alkylamine with this unreacted Reason, and it becomes a cause of a fall of storage stability in order to react to an isocyanate.

[0050]As for reaction temperature, it is desirable in solvents, such as toluene and xylene, to carry out under flowing-back conditions. As for reaction time, it is desirable to consider it as 6 to 24 hours, and

it is desirable to consider it as 8 to 12 hours especially. A Reason for having made reaction time into this range is that a reaction mixture will color in less than 6 hours if it is because the reaction is imperfect and exceeds 24 hours. It is preferred to perform a reaction in the usual atmosphere. N-hydroxyalkyl oxazolidine which distills off under decompression of superfluous aldehyde or ketone, and is expressed with the above-mentioned formula 4 after ending reaction is obtained.

[0051]A polyisocyanate compound is an organic group polyisocyanate which it has, and For example, polyhydric alcohol classes, such as glycerin, hexanetriol, trimethylolpropane, or a polypropylene glycol. The Para Feni range isocyanate, tolylene diisocyanate, tetramethylene diisocyanate, Hexamethylene diisocyanate, xylenediisocyanate, octadecyl diisocyanate. Naphthalene diisocyanate, 4, 4'-diphenylmethane diisocyanate, A resultant with isophorone diisocyanate, such denaturation articles, etc., Or it can obtain by making diisocyanate compounds, such as tetramethylene diisocyanate and hexamethylene diisocyanate (HDI), quantify three times under existence of a catalyst, and making an isocyanurate ring form. On the occasion of a reaction with N-hydroxyalkyl oxazolidine of the formula 4, these polyisocyanate compounds can be used alone and two or more sorts may be used together.

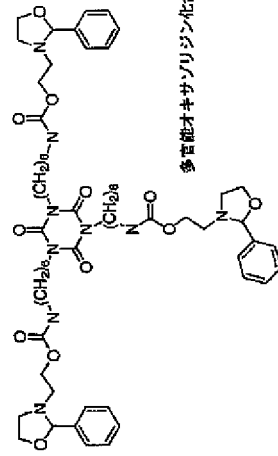
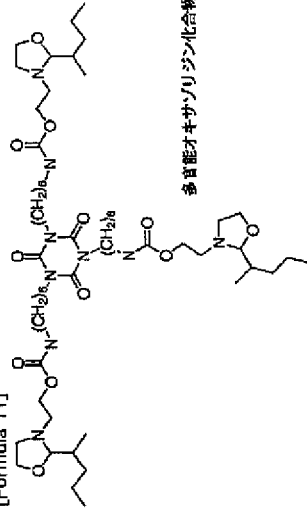
[0052]An oxazolidine compound which has three or more oxazolidine rings in one molecule is compounded by making a polyisocyanate compound react to N-hydroxyalkyl oxazolidine expressed with the formula 4 under ordinary pressure with reaction temperature of 50 °C - about 100 °C. Solvents, such as toluene and xylene, may be used in order to lower viscosity in the case of composition.

[0053]A quantitative ratio of N-hydroxyalkyl oxazolidine and a polyisocyanate compound is good for a polyisocyanate compound to make it react at 1 mol per 1 mol of hydroxyl of N-hydroxyalkyl oxazolidine.

[0054]As an example of a compound of having three or more oxazolidine rings, the polyfunctional oxazolidine compound (1), (2) expressed with a following formula is mentioned to such one molecule.

[0055]

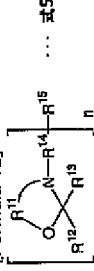
[Formula 11]



[0056]As other examples of an isocyanate oxazolidine compound, the compound expressed with the following formula 5 can be shown.

[0057]

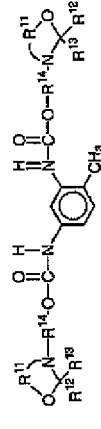
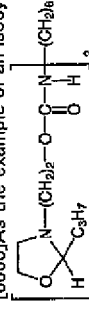
[Formula 12]



[0058]Here  $R^{11}$  --- the carbon numbers 2-6 --- desirable --- the carbon numbers 2-3 --- more --- desirable --- the alkylene group of the carbon number 2 --- it is  $R^{12}$  and  $R^{13}$  are a hydrogen atom, a with a carbon numbers of one or more alkyl group, an alicyclic alkyl group of the carbon numbers 5-7, or an aryl group of the carbon numbers 6-10 independently, respectively. As for  $R^{14}$ , it is preferred that it is an aryl group including the alkylene group of the carbon numbers 2-6, an aryl group, the alkylene group of the carbon numbers 2-6 including a urethane bond, or a urethane bond, and is the alkyl group or aryl group of the carbon numbers 1-5 which has a urethane bond.

[0059] $R^{15}$  is a basis obtained by removing an isocyanate group from n polyisocyanates, and should just form the skeleton of an isocyanate compound. It is preferred that it is a compound used as the skeleton of diisocyanate or tri-isocyanate compound, n is an integer of 1-4 and it is preferred that it is 2 or 3. The hardened material which was able to balance tensile strength and a tensile pace of expansion especially as n is 2 or 3 is obtained. If 3 is exceeded, it will become it is hard and weak, and hardening will become insufficient if it is less than two.

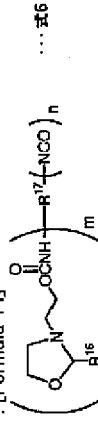
[0060]As the example of an isocyanate oxazolidine compound, [Formula 13]



イソシアネートオキサゾリジン化合物 (2)

Polyfunctional oxazolidine, such as which TDI base, a MDI base, a HDI base, and a HDI base, etc. are mentioned, and commercial items, such as the Bayer hardener OZ, can be used.

[0061]Other examples with a preferred isocyanate oxazolidine compound are the following formulas 6. : [Formula 14]



(as for  $R^{16}$ , the integer of 1-6 and n of the residue and m which are obtained from organic polyisocyanate except for an isocyanate group as for five or more aliphatic hydrocarbon groups with a number of carbon atoms, and  $R^{17}$  are the integers of 0-4 among a formula.) --- it is an oxazolidine compound shown.

[0062]As for  $R^{16}$ , five or more carbon atom numbers are an aliphatic hydrocarbon group with 5-15 carbon atoms preferably among the above-mentioned formula. For example, n-pentyl, 2-methylpentyl, 3-methylpentyl, 3,5,5-trimethyl pentyl, n-heptyl, n-octyl, n-nonyl, n-deca nyl, n-undecanyl, n-dodecanyl, n-trideca nyl, n-tetradeca nyl, etc. are mentioned. Especially, a case with 5-10 carbon atoms is preferred. And substituent of hydrolysis of a position of  $R^{16}$  is [ both substituents ] too quick in aliphatic hydrocarbon, and storage stability is bad. Hydrolysis is slow in  $R^{16}$  being an aromatic

group, and hardenability is bad. Hydrolysis is comparatively quick in the number of carbon atoms at four or less, and storage stability is bad. Although there are some which indicate a compound etc. whose R<sup>16</sup> is an alkyl group with 1-6 carbon atoms as an oxazolidine compound conventionally, there is no art of recognizing a difference in an effect as a latent curing agent by the difference in a carbon number within the limits of this concretely.

[0063]R<sup>17</sup> may be residue obtained from organic polyisocyanate except for an isocyanate group, and aliphatic series and alicyclic and aromatic any may be sufficient as it. For example, aromatic groups, such as tolylene, diphenylmethane, phenylene, and polymethylene polyphenylene. These carbodiimide denaturation groups or an isocyanurate denaturation group is mentioned to aromatic aliphatic groups, such as alicyclic hydrocarbon groups, such as aliphatic groups, such as hexamethylene, and isophorone, and xylene, and a pan, and it is used for them as one sort or two sorts or more of such combination.

[0064]As for n, it is preferred an integer of 1-6 and that it is 2-3 especially in respect of hardenability and the physical properties of a hardened material. As for n, it is preferred an integer of 0-4 and that it is 0-2 especially in respect of hardenability.

[0065]A manufacturing method of an isocyanate oxazolidine compound shown by the formula 5 compounds N-hydroxyethyl oxazolidine shown with the following formula 7 from \*\* diethanolamine and corresponding aldehyde, [Formula 15]

... 式7



(R<sup>18</sup> are five or more aliphatic hydrocarbon with a number of carbon atoms among a formula.) [0066]\*\* N-hydroxyethyl oxazolidine and organic polyisocyanate which are shown by the obtained formula 7 can be made to be able to react, and it can compound. Beforehand, when N-hydroxyethyl oxazolidine can be obtained, it is only above process \*\* and an expected isocyanate oxazolidine compound can be obtained. \*\* Make a reaction react under existence of organic solvents, such as benzene, toluene, and xylene, as the reaction temperature of 70-150 \*\*, and a solvent. A reaction mixture is refluxed under an oil bath after ending reaction for 5 to 10 hours. The reaction of \*\* mixes N-hydroxyethyl oxazolidine and organic polyisocyanate, is 60-90 \*\* and is made to react for 5 to 10 hours. Temperature may be changed in the middle of a reaction if needed.

[0067]As aldehyde used, n-hexanal, 2-methylpentanal, 2-methylheptanal, n-octanal, 3,5,5-trimethyl hexanal, n-decanal \*\*n-undecanal, n-dodecanal, n-tridecanal, n-tetradecanal, n-pentadecanal, etc. are mentioned, and it is available as a commercial item in such aldehyde.

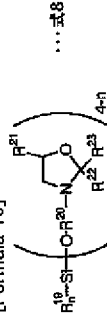
[0068]As organic polyisocyanate used in order to compound an isocyanate oxazolidine compound, it is usable in both [ aliphatic series and ] alicyclic and aromatic. For example, 2, 4-tolylene diisocyanate, 2, 6-tolylene diisocyanate, 4, 4'-diphenylmethane diisocyanate, 2, 4'-diphenylmethane diisocyanate, p-phenylene diisocyanate, aromatic polyisocyanate [ such as polymethylene polyphenylene polyisocyanate, ]; — aliphatic series polyisocyanate [ such as hexamethylene diisocyanate ]; — alicyclic polyisocyanate [ such as isophorone diisocyanate ]; — as for xylene diisocyanate etc., aromatic aliphatic series. Polyisocyanate; and these carbodiimide denaturation, or isocyanurate denaturation polyisocyanate is mentioned, and it is used as one sort or two sorts or more of such combination.

[0069]An isocyanate oxazolidine compound produced by making it above has the characteristic of being able to adjust physical properties variously.

[0070]Other examples with a preferred ingredient (C) are oxazolidine silylether, For example, it is compoundable by the reaction etc. of oxazolidine and a halogenation silyl compound which are obtained by the reaction of oxazolidine and alkoxyisilane containing a (i) hydroxyl group, or have a (ii) hydroxyl group. By making a titanium alkoxide, aluminum alkoxide, or a divalent tin compound (Sn<sup>2+</sup>) into a catalyst, it is 40-160 \*\* and a reaction of this inner (i) is especially performed at 80-140 \*\*. preferably. It may add as it is, or a catalyst may be melted and used into a solution of organic solvents, such as xylene. As for especially the amount of such catalyst used, it is preferred that it is 0.1 to 2 mass part 0.01 to 5 mass part to oxazolidine 100 mass part in respect of purity of reaction time and output.

[0071]As for such oxazolidine silylether, it is preferred that it is a compound shown with the following formula 8.

[Formula 16]



n is an integer of 0-3 among a formula.

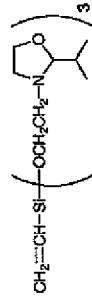
[0072]An alkyl group in which R<sup>19</sup> has a hydrogen atom and number of carbon atoms 1-12 piece, An alkoxyalkyl group, an alicyclic group, an alkoxy group, an acyloxyalkyl group, An amino alkyl group or an mercapto alkyl group, A vinyl group, a phenyl group, An amino group etc. are mentioned, for example, a methyl group, an ethyl group, a vinyl group, a meta-acyloxypropyl group, an epoxycyclohexyl group, a glycidoxy propyl group, an aminoethyl group, an aminopropyl group, a phenyl group, an amino group, and an mercaptopropyl group are illustrated. When n is two or more, an R<sup>19</sup> group may be independently another basis respectively, or may be the same basis.

[0073]As for R<sup>20</sup>, it is preferred an alkyl group of the carbon number 2 or 3 and that they are an ethyl group and an isopropyl group especially. As for R<sup>21</sup>, it is preferred that they are a hydrogen atom or a methyl group. R<sup>22</sup> and R<sup>23</sup> are the hydrocarbon groups of a hydrogen atom or the carbon numbers 1-20 independently respectively. Preferably [ that they are 3-12 carbon atoms ] and specifically, Alkoxyphenyl groups, such as an isopropyl group, an isopentyl group, and a phenyl group, for example, a methoxyphenyl group etc., are mentioned, and it is preferred that one of R<sup>22</sup> and the R<sup>23</sup> is a hydrogen atom especially in respect of storage stability and hardenability.

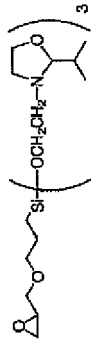
[0074]Oxazolidine silyl ether compound (1) - (7) etc. an example is indicated to be with a following formula are mentioned.

[0075]

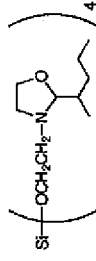
[Formula 17]



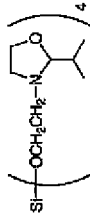
オキサゾリジンシリルエーテル化合物 (1)



オキサゾリジンシリルエーテル化合物 (2)



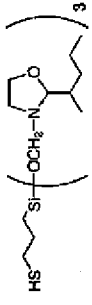
オキサゾリジンシリルエーテル化合物 (3)



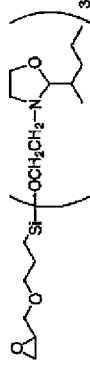
オキサゾリジンシリルエーテル化合物 (4)

[0076]

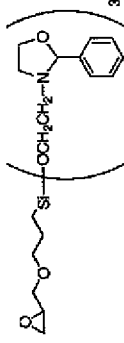
[Formula 18]



オキサゾリジンシリルエーテル化合物 (5)



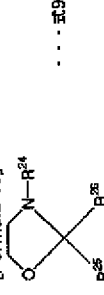
オキサゾリジンシリルエーテル化合物 (6)



オキサゾリジンシリルエーテル化合物 (7)

[0077] The oxazolidine compound furthermore suitably used as an ingredient (C) of this invention is a compound shown with the following formula 19.

[Formula 19]



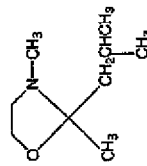
[0078] R<sup>24</sup> is an aliphatic hydrocarbon group which has with a carbon numbers of one or more straight chain shape or branched chain, for example, shows an alkyl group, an alkenyl group, and an alkylene group here. R<sup>25</sup> and R<sup>26</sup> show the hydrocarbon group of a hydrogen atom or the carbon numbers 1-20 independently respectively. These desirable examples are shown below.

[0079]

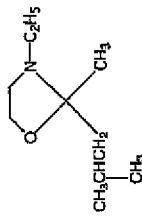
[Formula 20]



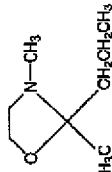
... 式10



... 式11



... 式12



[0080]The content of the (C) oxazolidine compound in the room-temperature-curing nature constituent of this invention is 1 - 80 mass part to (B) epoxy resin 100 mass part, and it is preferred that it is 5 - 40 mass part. Physical properties or hardenability of an organic polymer are not spoiled as it is this range.

[0081]The room-temperature-curing nature constituent of this invention shows the Reason for excelling in adhesion manifestation nature. In the room-temperature-curing nature constituent of this invention, when the (B) epoxy resin which both separated gradually and was mainly separated from the state where (A) organicity polymer and the (B) epoxy resin are distributing hardens, an adhesive property is revealed. On the other hand, hydrolysis generates an imino group and a hydroxyl group under existence of humidity (water), the imino group reacts to the epoxy group which the (B) epoxy resin has, and the (C) oxazolidine compound stiffens the (B) epoxy resin. Although hardening of the (B) epoxy resin by an imino group is not necessarily quick under a room temperature, when the hardenability under the room temperature of (A) organicity polymer is taken into consideration, it is a suitable speed. Thus, since the balance of hardening of (A) organicity polymer and the (B) epoxy resin is preferred, the adhesion manifestation nature of the room-temperature-curing nature constituent of this invention becomes the outstanding thing.

[0082]The (D) silanol condensation catalyst used for a room-temperature-curing nature constituent of this invention, For example, titanate system coupling agents, such as tetrabutyl titanate and tetrapropyl titanate; Tin carboxylate, for example, dibutyltin dilaurate, dibutyltin maleate, and dibutyltin diacetate. Tin octylate, naphthenic acid tin, a reactant of dibutyl tin oxide and phthalic ester, Organic tin compounds, such as dibutyl tin diacetyl acetate, aluminum tris acetylacetate, Chelate compound, such as organoaluminum compound; zirconium tetra acetylacetate, and titanium tetra aluminumtrithylacetate and diisopropoxy aluminum ethylacetate, and titanium tetra acetylacetate; lead octylate is mentioned. These may be used independently and may use two or more sorts together.

[0083]As for content of the (D) silanol condensation catalyst in a room-temperature-curing nature constituent of this invention, it is preferred that it is 0.1 - 20 mass part to (A) organicity polymer 100 mass part, and it is more preferred that it is 1 - 10 mass part. It becomes what was excellent in working life under a room temperature, and balance of the hardening characteristic in it being this range.

[0084][E] amine system co-catalyst used for a room-temperature-curing nature constituent of this invention, For example, butylamine, octylamine, lauryl amine, dibutyl amine, Monoethanolamine, diethanolamine, triethanolamine, Diethylenetriamine, triethylenetetramine, oleylamine, Cyclohexylamine, benzylamine, diethylamino propylamine, Xylylene diamine, triethylenediamine,

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guanidine, diphenylguanidine, 2,4,6-tris(dimethyl aminomethyl) phenol, morpholine, N-methylmorpholine, 2-ethyl-4-methylimidazole, Amine compounds, such as the 1,8-diazabicyclo (5.4.0) undecene 7 (DBU), and these amine compounds, and a salt with carboxylic acid etc.; low-molecular-weight-polyamide resin obtained from superfluuous polyamine and polybasic acid is mentioned. These may be used independently and may use two or more sorts together.

[0085]As for content of (E) amine system co-catalyst in a room-temperature-curing nature constituent of this invention, it is preferred that it is 0.01 - 5 mass part to (A) organicity polymer 100 mass part, and it is more preferred that it is 0.1 - 5 mass part. It becomes what was excellent in balance of the hardening characteristic with working life in it being this range.

[0086]A room-temperature-curing nature constituent of this invention may contain a cross linking agent, a bulking agent, a plasticizer, stabilizer, colorant, etc. if needed, in order to adjust viscosity, physical properties, etc. in addition to the above-mentioned essential ingredient. (F) (1)-ethylhexanoic acid especially, (2) It is preferred to contain at least one oxazolidine ring breakage accelerator chosen from a group which consists of a mixture or an addition of ORUTOGI acid ester and (3) ORUTOGI acid ester, and a p-toluenesulfonic-acid monoisocyanate. With these (F) oxazolidine ring breakage accelerators, ring opening reaction of an oxazolidine ring of the (C) oxazolidine compound is promoted, and the hardenability of the (B) epoxy resin improves remarkably. [0087]2-ethylhexanoic acid is known as a ring breakage accelerator of an oxazolidine ring, and can be conveniently used also in this invention.

[0088]ORUTOGI acid ester is a compound expressed with the following formula 13.

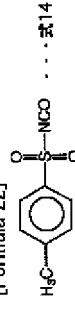
[Formula 21]



... 式13

[0089] $R^{27}$ ,  $R^{28}$ , and  $R^{29}$  express an alkyl group or an aryl group here. Methyl orthoformate, ethyl orthoformate, etc. can be illustrated as ORUTOGI acid ester. By hydrolyzing, ORUTOGI acid ester supplies acid and, thereby, can act as a catalyst of the ring opening reaction of an oxazolidine ring. [0090]Although a p-toluenesulfonic-acid monoisocyanate is a compound expressed with the following formula 14, and phosgene can be used for it or it can obtain it with a publicly known isocyanate synthetic method by Hofmann degradation, it can use commercial items, such as additive Ti by the Sumitomo Beyer urethane company. The ORUTOGI acid ester which is mixed with a p-toluenesulfonic-acid monoisocyanate, or is made to add can use the same thing as a case where it uses by independent [ which was mentioned above ].

[Formula 22]



... 式14

[0092]As for the content of (F) oxazolidine ring breakage accelerator in the room-temperature-curing nature constituent of this invention, it is preferred that it is 0.1 - 100 mass part to (C) oxazolidine compound 100 mass part, and it is more preferred that it is 1 - 50 mass part. Desirable hardened material nature is obtained with it being this range.

[0093]The ingredient which may be added when required in addition to the (F) ingredient used suitably for the essential ingredient of this invention and this invention is illustrated below.

[0094]a bulking agent — fumed silica and calcium carbonate (precipitated calcium carbonate.) Heavy calcium carbonate and a thing which carried out the surface treatment of these with fatty acid, resin acid, or fatty acid ester, Carbon black, clay, talc, titanium oxide, quicklime, kaolin, zeolite, diatomaceous earth, VCM/PVC paste resin, glass balloons, a vinylidene-chloride-resin balloon, an acrylonitrile methacrylonitrile resin balloon, etc. are mentioned, and it is independent, or can be mixed and used.

[0095]A plasticizer is not limited especially if it dissolves with (A) organicity polymer with process oil or other hydrocarbon, and it is [ plasticizer ] usable in various kinds of publicly known plasticizers. For example, dibutyl phthalate, diheptylphthalate, di(2-ethylhexyl) phthalate, Phthalic ester, such as

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butyl/benzyl phthalate and butyl phthalyl butyl glycolate; Diocetyl adipate, Non-aromatic dibasic acid ester species, such as dioctyl sebacate; Diethylene glycol dibenzoate, Ester species of polyalkylene glycols, such as triethylene glycol dibenzoate; Tricresyl phosphate, phosphoric ester [ such as tributyl phosphate, ], — chloroparaffin; — alkyl diphenyl; — hydrocarbon oil [ such as partially-hydrogenated terphenyl ]; — process oil; — alkylbenzenes are mentioned. Especially, using process oil has preferred compatibility with (A) organicity polymer from a good point. Although it may add apart from (A) organicity polymer, since mixing with (A) organicity polymer beforehand becomes viscosity suitable for workability, a plasticizer is preferred. As for content of a plasticizer in a room-temperature-curing nature constituent of this invention, it is preferred that it is 30 – 200 mass part to (A) organicity polymer 100 mass part, and it is more preferred that it is 30 – 150 mass part. [0096]As for stabilizer, a hindered phenol system compound and a triazole compound are mentioned, for example. As for colorant, a titanium white, carbon black, and red ochre are mentioned, for example.

[0097](A) organicity polymer whose room-temperature-curing nature constituent of this invention is an essential ingredient, for example, (B) It is obtained an epoxy resin, the (C) oxazolidine compound, the (D) silanol condensation catalyst, (E) amine system co-catalyst, and if needed by carrying out stirring mixing of (F) oxazolidine ring breakage accelerator and the other additive agents.

[0098]A room-temperature-curing nature constituent of this invention may reveal an outstanding adhesive property also to a hardened material of sealant, such as an aluminum plate or not only a glass plate but what is called a difficulty bonded steel sheet with which acrylic electropainting, fluoride paint, etc. were performed, and silicone series sealant. Therefore, it is suitably used as sealant of various building materials in which a hardened material of sealant, such as a steel plate in which acrylic electropainting, fluoride paint, etc. were performed, and silicone series sealant, is used. [0099]A room-temperature-curing nature constituent of this invention can also be made into which mode of two-component type sealant or 1 liquid type sealant. It can be determined in view of a use, description of (A) organicity polymer to be used, etc. two-component type or 1 liquid type any are used. When considering it as two-component type sealant, it is preferred to make the (C) oxazolidine compound contain in the hardening agent side.

[0100]The room-temperature-curing nature constituent of this invention can also use a primer together in the case of use, and a more outstanding adhesive property can be made to reveal. Since a thing containing an amino group content silane coupling agent is excellent in adhesion manifestation nature as a primer, it is desirable.

[0101]An amino group content silane coupling agent specifically, A conventionally publicly known silane coupling agent containing an amino group can be used. For example, gamma-aminopropyl trimethoxysilane, gamma-aminopropyl triethoxysilane, gamma-aminopropyl methyl dimethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane, gamma-ureido methyl dimethoxysilane, N-(beta-aminoethyl)-gamma-aminopropyl triethoxysilane, gamma-ureido propyl propyltrimethoxysilane, gamma-aminol propyltrimethoxysilane, N-phenyl-gamma-aminopropyl trimethoxysilane, etc. are mentioned. These may be used independently and may use together these two or more sorts.

[0102]

[Example]Although working example is given to below and this invention is explained more concretely, this invention is not limited to following working example.

Stirring mixing of the material shown below in <preparation of a room-temperature-curing nature constituent> was carried out using 5L planetary (omnipotent stirrer) by the quantitative ratio shown in the 1st table, and the base resin and the hardening agent of two-component type sealant used as the room-temperature-curing nature constituent which uses as the main ingredients the organic polymer which has a reactive silicon group were prepared.

(1) Main agent component \*\* (A) organicity polymer : P IB oligomer, EPION505S. The process oil of the Kaneka Corp. make, the average molecular weights 20000, and 33 mass % Content \*\* (B) epoxy resin i bisphenol-type-epoxy-resin:Epicoat 828, oil recovery shell chemicals company make, The weight per epoxy equivalent 184 – a 194ii polysulfide type epoxy resin : FLEP50, Toray Industries thiolol company make \*\* bulking agent:fatty acid processing calcium carbonate, Culi fine 200, \*\* plasticizer by Maruo Calcium Co., Ltd.: Process oil, PS-32, Idemitsu Kosan \*\* water (2) hardening agent-component \*\* (C) oxazolidine compound IMS-PLUS, the product made by ANGUS, and chemical

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constitution formulas are expressed with said formula 11. The hardener OZ, \*\* (D) silanol condensation catalyst by a Beyer company : ii) Tin octylate, Neo SUTAN U-28, a Japanese East Chemicals \*\* (E) amine system co-catalyst : Lauryl amine, Firmin 20D, \*\* (F) oxazolidine ring breakage accelerator i) by Kao Corp.-ethylhexanoic acid ii) ORUTOQI acid ester : The permanent wave flow OF. Japanese treasure chemicals company make iii) p-toluenesulfonic-acid monoisocyanate: ORUTOGI acid ester and a p-toluenesulfonic-acid monoisocyanate were used, after [ which are additive Ti (Ad-Ti) and the Sumitomo Beyer urethane company make ] carrying out stirring mixing beforehand and considering it as a mixture or an addition.

[0103]

[Table 1]

第 1 表

		比較例						
		1	2	3	4	5	6	7
主	(A) 有機重合体	100	100	100	100	100	100	100
	可塑剤	100	100	100	100	100	100	100
	充填剤	150	150	150	150	150	150	150
剤	ビスフェノール型エポキシ樹脂	5	5	5	5	5	5	5
	ポリシリカフィラー型エポキシ樹脂	5	5	5	5	5	5	5
	水	5	5	5	5	5	5	5
(E) アミン系助触媒		0.5	0.5	0.5	0.5	0.5	0.5	0.5
(D) シラノール縮合触媒		3	3	3	3	3	3	3
化	オキサゾリンMS-PLUS	0	2.5	5	0	0	0	4
	オキサゾリンハナード-OZ	0	0	0	3	3	3	0
剤	2-エチルヘキサノール酸	0	0	0	0	0.5	0	0
	オルトギ酸エステル	0	0	0	0	0	0.2	0
	ポロトエンズルホン酸モノソシアネート	0	0	0	0	0	1	0

[0104]Stirring mixing of the material shown below in <preparation of a primer composition> was carried out by the quantitative ratio shown in the 2nd table, and the primer compositions A and B were prepared

Organic solvent \*\* n-hexane \*\* toluene (2) silicone resin : (1) Poly alkyl siloxane, X-40-2134, Shin-Etsu Chemical Co., Ltd. make (3) amino-group content silane coupling agent:N-(beta-aminoethyl)-gamma-aminopropyl trimethoxysilane, A1120, the Nippon Unicar curing catalyst (4): Titanate, TPT-100, Nippon Soda Co., Ltd. make (5) saturated-hydrocarbon system polymer :P The process oil of IB oligomer, EPION103S, the Kaneka Corp. make, the weight average molecular weight 5000, and 23 mass % is contained. [0105]

[Table 2]

第 2 表

	プライマー-A	プライマー-B
n-ヘキサン	90	90
トルエン	10	10
有機重合体	0	10
シリコン樹脂	2	1
アミノ基含有シランカップリング剤	7	7
硬化触媒	4	2.5

[0106]<Adhesive examination> The obtained primer composition A or B was applied to the surface of plate-like adherend by BEMCOT. As adherend, an aluminum plate, the glass plate, the acrylic electropainting steel plate, the fluoride coated steel sheet, and the silicone series sealant hardened material were used. After applying each primer composition under ordinary temperature on these adherends and neglecting it for 60 minutes, each room-temperature-curing nature constituent was

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placed about 1 cm in diameter in the shape of a bead, and care of health 50 \*\* 20 \*\* for three days and for three days was performed. Then, it is based on the simple adhesive property examination (Japanese sealing material industrial meeting "structural sealing material handbook" p.109) by knife cutting, and is friction test \*\*\*\*\* (a 0-degree friction test and a 90-degree friction test) about a 0 degree direction and a 90-degree direction as a tensile direction. The adhesive property was evaluated like O-sealant destruction, \*\*thin layer exfoliation, and x:interface exfoliation.

[0107]A result is shown in the 3rd table. The room-temperature-curing nature constituent (working example 1 and 2) of this invention reveals the outstanding adhesive property also to which adherend of glass, an acrylic electropainting steel plate, a fluoride coated steel sheet, and a silicone series sealant hardened material so that clearly from the 3rd table. When using the primer (primer B) inferior to adhesion manifestation nature, the outstanding adhesive property can be made to reveal by adding (F) oxazolidine ring breakage accelerator further, or choosing the suitable (C) oxazolidine compound. On the other hand, the conventional room-temperature-curing nature constituent (comparative example 1) which contains (A) organicity polymer and the (B) epoxy resin, and does not contain the (C) oxazolidine compound does not reveal sufficient adhesive property.

[0108]

[Table 3]

第 3 表

室温硬化性組成物	比較例						
	1	2	3	4	5	6	7
プライマー組成物	A	A	B	B	B	B	B
はく離試験 (90°はく離/0°はく離)							
アルミニウム板	O/x	O/Δ	O/O	O/x	O/Δ	O/O	O/O
ガラス板	O/x	O/Δ	O/O	O/x	O/Δ	O/O	O/O
アクリル電着銅板	Δ/x	O/Δ	O/O	Δ/x	Δ/Δ	O/Δ	O/O
フッ素焼付銅板	Δ/x	O/Δ	O/O	Δ/x	Δ/Δ	O/O	O/O
シリコン系シーラント硬化物	—	—	x/x	Δ/x	Δ/x	Δ/Δ	Δ/O

[0109]

[Effect of the Invention]The room-temperature-curing nature constituent of this invention reveals sufficient adhesive property also to the hardened material of sealant, such as a difficulty adhesive property steel plate in which acrylic electropainting, fluoride paint, etc. were performed, and silicone series sealant.

[Translation done.]